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Complexes of Co(II), Ni(II), Cu(II), Mn(II) & U(VI) with Benzilic, α-Phenyllactic & Mandelic Acids

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Complexes of Co(II), Ni(II), Cu(II), Mn(II) and U(VI) with benzilic, α-phenyllactic and mandelic acids have been studied both in solution and solid states. The equilibrium constants have been calculated; except for uranyl complexes because of the simultaneous existence of both 1:1 and 1:2 complexes in solution. The stoichiometry of the complexes is 1:2 (metal-ligand) as revealed by Jobs and the mole ratio methods. Copper mandelate and uranyl-α-hydroxy-carboxylates have been isolated in the solid state. From the study of magnetic moment and IR spectra, possible structures for the solid complexes have been suggested.

IN continuation of the earlier work[1-5] from our laboratory on the chelates of Fe(II and III), Co(II), Ni(II) and Cu(II) with benzilic acid, the chelates of bivalent Fe, Co, Ni, Cu, Mn and of U(VI) have now been studied both in solution and solid states.

Materials and Methods

Cu(II), Co(II), Ni(II), Fe(II) and Mn(II) sulphates used were of either AnalaR or GR grades. The metal solutions prepared in doubly distilled water were standardized by the usual methods. Mandelic acid (Mallincrodt, USA) was recrystallized twice from water and then neutralized with caustic soda. The details of benzilic and *a*-phenyllactic acids have been mentioned earlier[5].

Electronic spectra were recorded on a Beckman DB model spectrophotometer. IR spectra in KBr were recorded on a Perkin-Elmer 337 model. TGA of copper mandelate was carried out in a derivatograph (MOM) under normal atmospheric environment. Gouy magnetic balance was employed for the determination of the magnetic susceptibility of solid complexes at 30° as described in our previous paper[4].

Carbon and hydrogen were analysed by micro-analytical method. Cu(II) was estimated by the iodometric method. The uranyl ion was determined gravimetrically after ignition to the oxide U_3O_8.

Cu(II) *and U*(VI) *complexes* — Aq. solutions of sodium mandelate and copper salt (2:1 molar ratio) were mixed together and stirred. Immediate precipitation occurred. The complex formed was filtered, washed and dried.

To uranyl nitrate solution (aq.) was added gradually the solution of the ligand with stirring. In the case of benzilate, at first a white precipitate appeared which on stirring dissolved giving an intense yellow colour. On the addition of excess of benzilate solution, a heavy yellow-coloured precipitate appeared immediately. For the appearance of yellow compound of α-phenyllactate and mandelate, the mixtures were kept standing for 3 hr. The yellow compounds were filtered, washed with water and ethanol, and dried in a vacuum desiccator. The results of elemental analyses of the complexes are presented in Table 1.

Results and Discussion

Composition and spectra of the complexes in solution — Different solutions of a metal and ligand in the ratios of 2:1, 1:1, 1:2, 1:3 and 1:4 were made. The total volume of each solution was kept fixed and in each case a sharp maximum has been found at 252 nm. The absorption maximum of the ligand has been observed at 258 nm.

The complexes of the bivalent metal ions studied have 1:2 (metal-ligand) stoichiometry as revealed by Job's as well as the mole ratio methods at 252, 258 and 265 nm.

Uranyl-benzilate complex exhibits maximum absorption at 258 nm, whereas both uranyl-α-phenyl-

TABLE 1 — ELEMENTAL ANALYSES OF THE SOLID COMPLEXES

Complexes	Colour	Found (%)			Calc. (%)		
		C	H	M	C	H	M
1. $UO_2(BZ)_2.2H_2O$	Yellow	44·93	4·02	34·62	44·38	3·43	35·27
2. $UO_2(PL)_2.2H_2O$	do	33·82	3·04	41·46	34·12	3·47	42·17
3. $UO_2(MA)_2.2H_2O$	do	32·25	3·23	43·87	31·73	2·97	44·13
4. $Cu(MA)_2.2H_2O$	Light blue	47·7	4·60	16·40	48·0	4·2	15·8

BZ = benzilate, PL = α-phenyllactate, MA = mandelate, M = UO_2^{++} (for 1-3) and M = Cu^{++} for 4.

lactate and uranyl mandelate complexes show maximum absorption at 252 nm. Although all the free hydroxycarboxylates absorb maximum at 258 nm, which is perhaps the characteristic of the phenyl radical, the complexes absorb with large extinction values. The molar extinction coefficients of benzilate, α-phenyllactate and mandelate complexes of all the metal ion except U(VI) are 4400 (258 nm), 3050 (252 nm) and 2878 (252 nm). The molar extinctions of uranyl nitrate at 252 and 258 nm are 960 and 820 respectively. The molar extinctions of free benzilate, α-phenyllactate and mandelate at 258 nm are 580, 259 and 192 respectively.

Mole ratio and Job's method of continued variation was also adopted in studying the composition of the yellow compound formed with uranyl ion in solution. The composition was found to be 1:1 (uranyl-ligand). At very low concentration ($0{\cdot}5 \times 10^{-3} M$), however, the composition obtained was 1:2 (uranyl-ligand). Since uranyl ions and ligands have considerable absorptions, a 9 mm spacer was inserted in the 1 cm cell to make measurements possible. The 1:1 and 1:2 compositions of the complexes were also corroborated by conductometric titration of uranyl solution with ligand solutions[5].

Effect of pH on the stability of uranyl complexes — The formation of the yellow complexes in solution was dependent on *p*H of the solution. The *p*H of the yellow-coloured solution was lowered gradually from 5 to 2·7 by the addition of $HClO_4$ and the spectra recorded. The yellow complex was stable in *p*H range 5·5 to 4·7 with λ_{max} at 345 and 450 nm remaining undisturbed. Below *p*H 4·6 the band at 345 was shifted to lower wavelength region (320 nm). Mandelate and α-phenyllactate complexes were stable in *p*H range 5·5 to 4·65 below which the yellow colour gradually disappeared.

Calculation of stability constants — The equilibrium constants of the complex forming reactions have been evaluated using Eq. (1).

$$\underset{(a-x)}{M^{2+}} + \underset{(b-2x)}{2LA^-} \overset{K}{\rightleftharpoons} \underset{(x)}{M.LA_2}$$

$$K = \frac{[x]}{[a-x][b-2x]^2} \qquad \ldots(1)$$

The extinction coefficients have been calculated as mentioned in our previous communication[4]. Extinctions of the metal solutions of Co(II) and Ni(II) were very low and hence neglected for the actual calculations of concentrations of their complexes.

Assuming

$$A_{total} = A_{complex} + A_{free\ ligand} + A_{free\ M^{2+}} \qquad \ldots(2)$$

$$= \epsilon_1 x + b\epsilon_2 - 2[x]\epsilon_2 + a\epsilon_3 - x\epsilon_3 \qquad \ldots(3)$$

where ϵ_1, ϵ_2 and ϵ_3 are the extinctions of the complex, the ligand and the metal ion respectively, the concentration of the complexes involving divalent metal ions and the ligands can be calculated from the equation

$$[x] = \frac{(A_{total} - b\epsilon_2 - a\epsilon_3)}{(\epsilon_1 - 2\epsilon_2 - \epsilon_3)} \qquad \ldots(4)$$

The calculation of equilibrium constants of the uranyl complexes could not be made because of the simultaneous existence of both 1:1 and 1:2 complexes in solution.

The equilibrium constants of different complexes are presented in Table 2. A linear relationship exists between logarithm of equilibrium constants of the complexes and atomic number as well as with the second ionization potential of the bivalent metal ions under study (Fig. 1). Mn(II) chelates, however, show little deviation.

Structure of the complexes — The Cu(II) complexes appear to have an octahedral geometry, where two water molecules occupy two positions of the octahedron. The structure may, therefore, be represented as $Cu(MA)_2, 2H_2O$. This was further supported by the infrared data of the solid complex in nujol mull. The principal infrared bands which appeared at 3100 cm^{-1} (w) 1630 cm^{-1} (s) and 1330 cm^{-1} (b, m), were due to the chelation through carboxylic and hydroxyl groups. In addition to these bands, another band appeared at 800 cm^{-1} (m), but absent in the free mandelic acid. The IR data thus suggests the presence of coordinated water molecules in the complex.

The TGA of yellow-coloured solid complexes of uranyl indicated the composition of uranyl-hydroxycarboxylates as 1:2. The yellow solids have very

TABLE 2 — STABILITY CONSTANTS AND FREE ENERGIES ($-\Delta G$) OF Mn(II), Fe(II), Co(II), Ni(II) AND Cu(II) COMPLEXES

{(a), [Metal(II)] = $3{\cdot}30 \times 10^{-4} M$, [benzilate] = $6{\cdot}67 \times 10^{-4} M$; (b), [Metal(II)] = $2{\cdot}50 \times 10^{-4} M$, [α-phenyllactate] = $5{\cdot}0 \times 10^{-4} M$; (c), [Metal(II)] = $3{\cdot}30 \times 10^{-4} M$, [mandelate] = $6{\cdot}67 \times 10^{-4} M$}

Complexes	*a*		*b*		*c*	
	Log K	$-\Delta G$ (kcal/mole)	Log K	$-\Delta G$ (kcal/mole)	Log K	$-\Delta G$ (kcal/mole)
Mn(II)	6·65±0·20	9·18±0·27	6·64±0·15	9·12±0·23	6·68±0·12	9·23±0·15
Fe(II)	6·15±0·18	8·58±0·22	—	—	—	—
Co(II)	6·03±0·08	8·42±0·12	6·99±0·14	9·66±0·19	7·01±0·20	9·69±0·24
Ni(II)	5·98±0·13	8·26±0·18	6·76±0·11	9·34±0·14	6·82±0·23	9·43±0·27
Cu(II)	5·88±0·16	8·22±0·22	6·49±0·17	8·97±0·21	6·68±1·5	9·24±0·20

The average of three values at wavelengths 252, 258 and 265 nm have been reported. Stability constants of Fe(II)-α-phenyllactate and mandelate could not be reported since the complexes are unstable; although within the inherent instability the mole ratio method indicated the complexes to be 1:2 (metal-ligand) stoichiometry ratio.

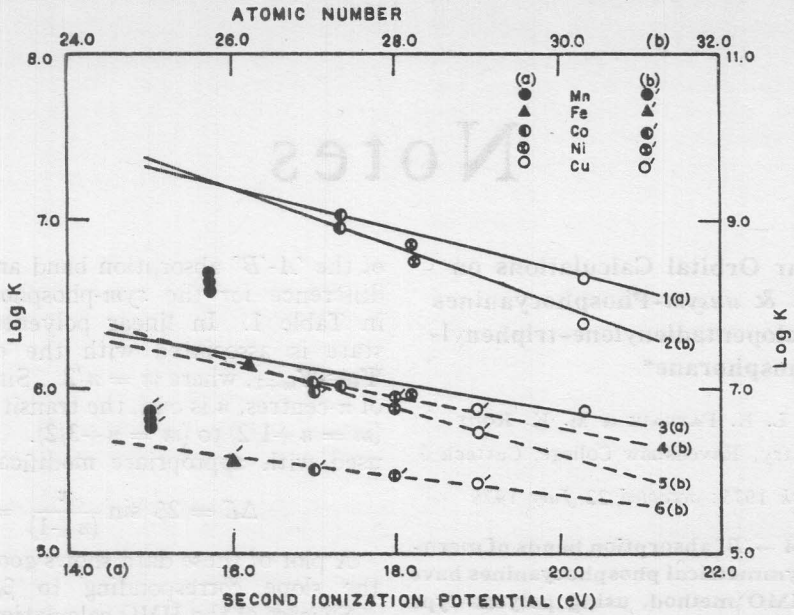

Fig. 1 — (a) Plot of second ionization potential against log K [1, Mandelate, 2, α-phenyllactate and 3, benzilate series respectively]; (b) Plot of atomic number against log K [4, Mandelate, 5, α-phenyllactate and 6, benzilate series respectively]

low solubility in water ($10^{-4}M$). The saturated solution of uranyl α-phenyllactate and mandelate exhibited maximum absorption at 252 nm. The yellow solids formed with excess ligands at pH 5·2 were definitely different from the intense yellow-coloured compounds formed in solution which were highly soluble in water. TGA and IR spectral analyses of solid complexes indicate the presence of two water molecules which perhaps occupy the zone outside the coordination sphere as mere water of hydration.

The room temperature magnetic moment (~303°K) of copper mandelate complex was found to be 1·9 BM as against the value of 1·68 BM obtained for copper benzilate complex. The theoretically expected value for the copper complex is 1·73 BM and therefore the present result was slightly higher than what was expected. The uranyl complexes were found to be diamagnetic.

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